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Anodic Dissolution of Non-Ferrous Metals in a Glycerate-Alkali Electrolyte

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Abstract. Studies have been conducted to assess the possibility of refining a lead collector containing precious metals, with the aim of obtaining lead using an economically viable and environmentally safe technology. A method of electrochemical selection in an alkaline glycerate electrolyte is proposed. The behavior of lead, silver and “silver crust” during anodic polarization in glycerate electrolyte was studied using the potentiodynamic method. “Silver crust” – type alloy of the following composition were used in this study, (wt.) %: 77.9 Pb, 12.76 Zn, 3.53 Ag, 0.50 Cu, Sb 0.90. The studies were carried out using the method of a rotating disk. Studied the patterns of anodic oxidation of lead and impurities in alkaline-water-glycerate electrolytes, depending on the concentration of sodium hydroxide and glycerol in the electrolyte, the potential sweep rate.

1. Introduction

Anodic dissolution of non-ferrous metals and alloys is accompanied by the formation of a film of poorly soluble products on the surface of the anodes. The result of this process is the passivation of the anode, further dissolution slows down or stops completely. Metals such as lead, antimony, tin show a greater tendency to passivation. For this reason, electrochemical refining of alloys containing these metals in appreciable amounts is almost impossible.

The refinement of argentiferous lead by the pyrometallurgical method is accompanied by the production of silver crust, where precious metals are concentrated. Silver crust mostly contains lead, zinc, copper, bismuth, iron, tellurium and some other metals [1–4]. Improving the technology of complex processing of this multicomponent ingoing material is relevant.

2. Current technologies

The main purpose in the processing of silver crust is the selection of the extraction of precious metals. Traditional technologies are based on the distillation of crust in electrode furnaces with the aim of rundown to 90% zinc. The resulting residue is additionally cupelled, gold and silver remain in the bath of the furnace. The resulting alloy is poured into molds and sent for refining [5–8].

An alternative method was engineered in 1956 [3]. In an electrolyte containing 80 g/l of Pb and 100 g/l of sulfamic acid, 95% of Pb is recovered into the cathode sediment and 100% of all precious metals are extracted into the slime. Energy consumption was 150 kWh on ton of lead. The slime yield was approximately 17% by weight of the dissolved part of the anode, the sludge contained 82% Ag; 0.1



Au; 3.5% Pb; 6.5% Cu; 3.5% Zn; 0.6% Bi and 11.3% Sb. Metals are more electropositive than lead, (almost all impurities), remain in the anode slime, only tin is deposited with lead.

The electrolyte based on fluorosilicic acid and silicofluoride lead has become widespread in the electrorefining of raw lead. The lead to be refined, after debonding, was cast into anodes in the form of plates. The resulting sludge contained, %: 12–20 Pb; 4–5 Ag; 6–15 Cu; 25–30 Sb; 9–15 As [3].

Known electroextraction of lead from nitric-acid solutions with obtaining cathodic sediment – metallic lead and anodic - lead dioxide. The anode is titanium, the cathode is lead. When the concentration in the electrolyte, mol/l: Pb 0.5 and HNO₃ 0.5 reached a current output of 94% without releasing nitrous gases. To reduce dendritic formation at the cathode, formic acid was added to the electrolyte in the amount of ~ 440 g on 1 ton of cathode lead [9, 20].

Anodic dissolution of alloys containing in addition to lead, antimony and stannic in significant quantities - more than 10%. Using these electrolytes is not possible, since stannic, even at room temperature, forms an oxide film on the alloy surface, which causes irreversible passivation, reduces the rate of anodic dissolution.

With the joint processing of some lead-containing products at JSC “Uralektromed”, when refining lead, silver crust of the following composition is obtained, in mass %: 78.58 Pb, 15.95 Zn, 0.47 Bi, 0.22 Cu, 0.36 Fe, 0.63 Te, 0.005 As, 0.008 Sb, 0.003 Sn, 0.006 Ni, 0.002 Al, 0.02 Ca, 0.01 Mg, 4.31 Ag [2]. Currently, measures are being taken to select a rational technology for the complex processing of such raw materials.

The purpose of this work is to create a cost-effective and environmentally friendly technology for the integrated extraction of valuable components from polymetallic alloys of reduced composition. Certain prospects in solving this problem have electrochemical selection in alkali-glycerate electrolyte [10–12]. According to [13], when using anodes made of an alloy of lead and antimony, anodic dissolution of both metals occurs under optimal conditions [14–15], but in some cases the surface of the anode is oxidized to lead dioxide, on which the reaction actually takes place.

3. Research methods

The specific task of the experiments was to study the laws of anodic polarization of the alloy and individual components in the electrolyte using the potentiodynamic method and the installation of a rotating disk electrode. This method was used to research specific action of polymetallic alloy and separate components in conditions of anodic polarization.

Electrodes from following metals were used in research: crust alloy, lead, antimony, tin, silver, copper and zinc. Chemical pure reagents were melted in an induction furnace and poured into graphite molds. The obtained cylindrical samples were processed to a diameter of 7 mm and pressed into fluoroplastic forms. The measurements were carried out by the method of a rotating disk using the Volta “EM-04” attachment, the rotation speed of 800 rpm at room temperature is 25 °C.

Anodic dissolution of metals was studied using an IPC-Pro galvanostat-potentiostat, setting the potential change interval from -0.2 to 2 Volts with a sweep rate 100 mV/s, since a dense passivation layer is formed at low speeds. Concentrations of alkali and glycerol in equal proportions were used: 25, 50, 100, 150 g/l. Silver chloride reference electrode was used. The measurements were carried out in an open cell without separation of the auxiliary (platinum) electrode and the reference half-cell of porous glass or membrane partitions [16–19].

4. Discussion of results

The working surfaces of the disk electrodes were carefully processed before the experiment. Figures 1–4 show the potentiodynamic curves of the alloy, lead and silver, obtained under these conditions.

It is most likely that for electrodes made of lead and an alloy based on it, a significant anodic current near the potential of 0 mV during polarization is associated with the formation of lead oxide, which begins in the cathode potential region (-800 mV). Oxygen evolution becomes visually noticeable from 900–1200 mV. With increasing alkali concentration, the potential of this reaction shifts to the negative region. In the potential range of 600–800 mV, a peak is observed which is characteristic of a deeper

oxidation of lead to dioxide. Under dynamic conditions of potential sweep, lead oxidation occurs at a satisfactory rate in the range of 200–800 mV at a speed of 100–200 mA/cm².

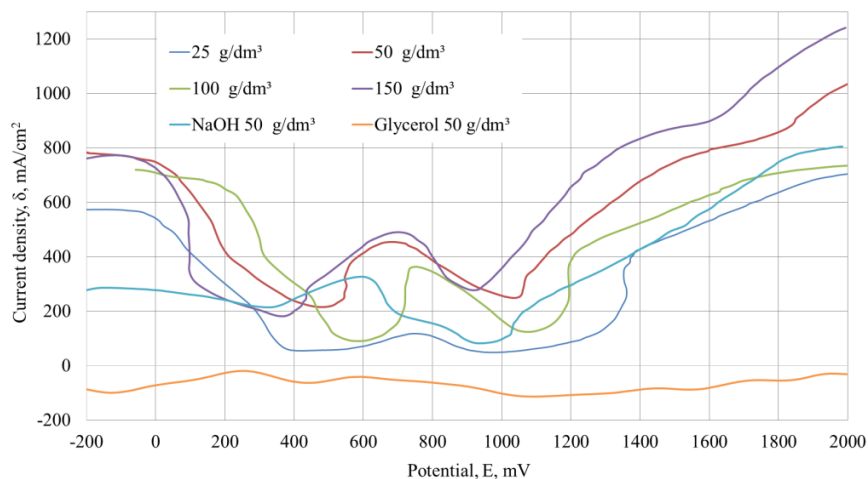


Figure 1. Polarization graphs of foam alloy.

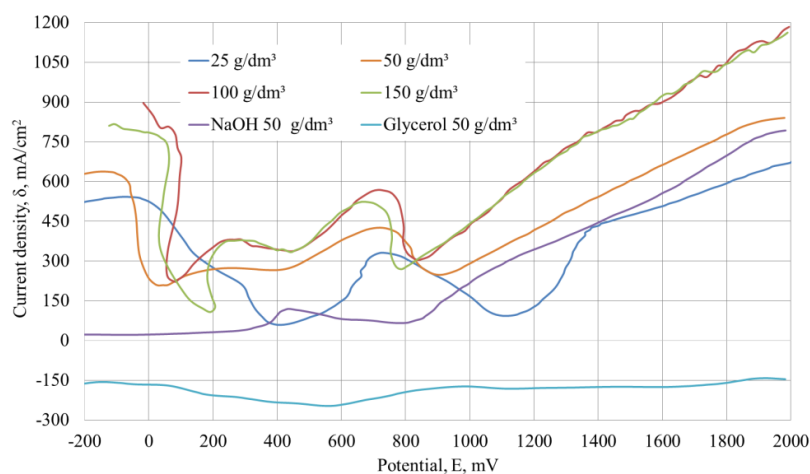


Figure 2. Polarization graphs of lead.

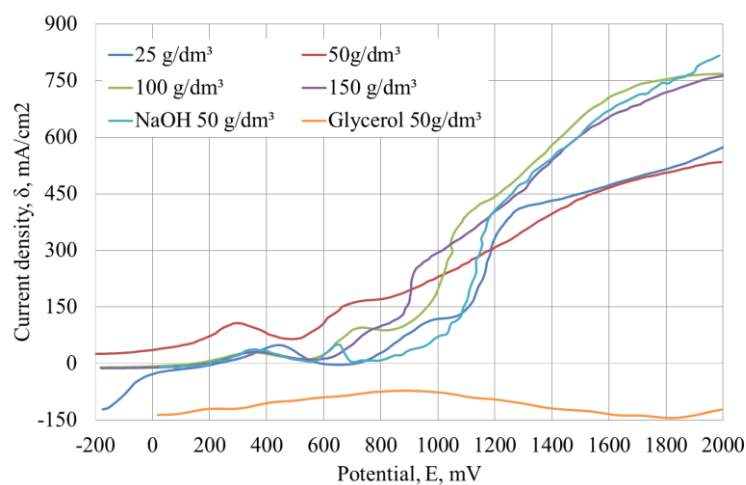


Figure 3. Polarization graphs of silver.

Silver in electrolytes alkali-glycerin is passivated, when measuring the disk was covered with loose black sediment, at the potentials of 700–900 mV, the beginning of oxygen evolution was observed. The current density of anodic oxidation of silver does not exceed 10–20 mA/cm². According to the XRD, the precipitate is represented by silver oxide.

With an increase in the velocity of the potential sweep, the beginning of the noted processes shifts to the region of more negative potentials. The optimum scanning speed, allowing to identify confidently differences in the behavior of the alloy components lies in the range from 50 mV/s to 150 mV/s.

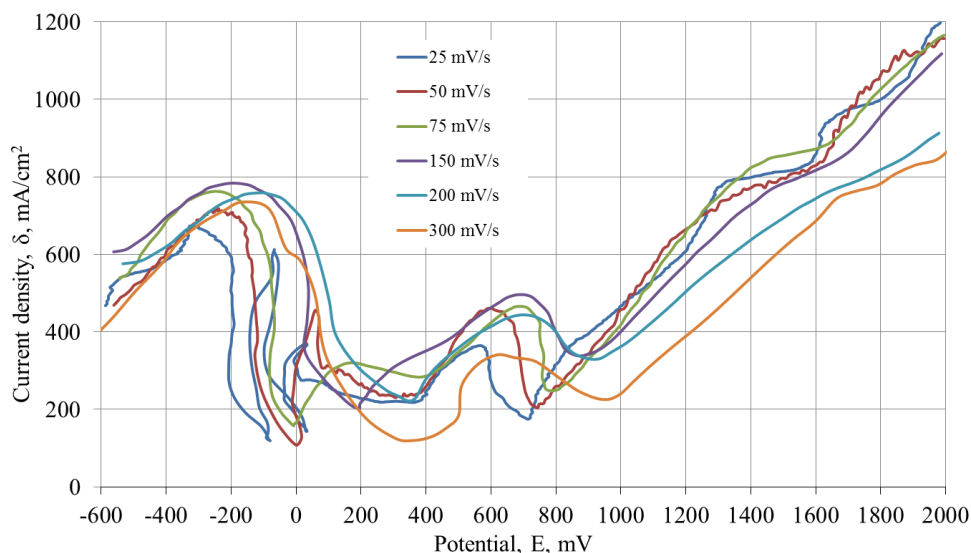


Figure 4. Polarization graphs of lead with different speed sweep at concentration 150 g/l alkali/glycerol.

The graph shows that increasing the sweep rate leads the current density to lower range. However, too low scanning speeds result in significant increase of experiment time and distortion of the curves. According to the graphic optimal scanning speed is situated between 75 mV/s and 200 mV/s, cause a scanning speed of experiments was 100 mV/s.

5. Conclusion

The area of confident oxidation of lead in the alkaline-glycerate electrolyte corresponds to the potentials of 300–800 mV.

For the lead-based polymetallic alloy (silver crust) area of anodic oxidation corresponds to the potentials of 700–800 mV.

The totality of the revealed regularities of the anodic polarization of polymetallic alloys gives reason to assume a confident transition to a solution of lead, antimony and tin, while silver, gold, tellurium are concentrated in the anode sludge.

Silver is oxidized to form an insoluble oxide, which forms the anode sludge. The issue of further research is determination of passivation process, influence on glycerol, electrolyte components, temperature, potential sweep and rotational disc speed.

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